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(54) Title: SHAPE MEMORY RUBBER COMPOSITION

(57) Abstract: Disclosed is a shape memory rubber composition, which is advantageous in terms of excellent shape memory performance, and having similar elastic force and hardness to a conventional rubber article, thus various designs and performance of articles being able to be obtained by altering the shape of articles. The shape memory rubber composition comprises a crystalline polyalkylene polymer, which has trans double bonds consisting of 60 % or more of its total double bonds, a melting point of 28 °C and a glass transition point of -80 °C; a rubbery polymer having crosslinkable points in polymer principal chains and side chains; a vulcanizing agent, being not crosslinked with said crystalline polyalkylene polymers but crosslinked with said rubbery polymers; and other additives.

SHAPE MEMORY RUBBER COMPOSITION

TECHNICAL FIELD

5 The present invention relates generally to a rubber composition having shape memory properties, which can be applied to rubber articles such as tires, shoes and so on, and, in particular, to a rubber composition mainly comprising trans double bonds-rich crystalline
10 polyalkylene polymers and amorphous rubber.

PRIOR ART

 There have been recently provided shape memory
15 materials comprising shape memory alloys and some shape memory polymers.

 The shape-memory polymer adopts a three-dimensional shape imposed under a condition a and even when changed to a quite different shape under another condition b,
20 restores the original shape under a condition c.

 Such shape memory polymers are exemplified by crystalline polymer crosslinked substances, for example, crystalline polyolefin crosslinked substances disclosed in U.S. Pat. No. 3,082,242, crystalline trans-isoprene
25 crosslinked substances disclosed in U.S. Pat. No. 3,139,468; and shape memory polymers having remarkably high molecular weight made by fixing physically twisted .

portions in superpolymers, for instance, polynorbornene based superpolymers disclosed in U.S. Pat. No. 4,831,094.

In this regard, the crystalline polymer substances can be crosslinked through vulcanization or curing reactions, because crosslinkable points such as double bonds are present in a polymer chain itself, along with crystal phases. As such, however, said substances show only properties of resin materials, such as very high hardness and low elastic force, and thus cannot be applied to rubbery elasticity-required articles. In addition, they suffer from poor weatherability and heat resistance caused by double bonds.

In the case of the shape memory polymers having remarkably high molecular weight, superpolymers have poor flowability and cannot utilize general molding processes, such as injection molding or extrusion molding for their manufacture. Also, double bonds having very high hardness of molding portion exist in superpolymers, which is thus disadvantageous in terms of low weatherability and heat resistance.

Meanwhile, Japanese Application Pat. No. Hei 1986-293214 refers to shape memory polyurethane elastic polymers. But the disclosed polymers have disadvantages of low shape-memory properties and high hardness, as in resin materials, attributable to thermosetting polymer properties of crosslinked molecules. In addition, U.S. Pat. Nos. 5,189,110 and 5,270,388 disclose thermoplastic

block copolymers, which have excellent heat resistance but low impact resistance and high hardness, thus being able to be applied as rubbery articles.

5

DISCLOSURE OF THE INVENTION

Accordingly, it is an object of the present invention to alleviate the problems as described above and to provide a shape-memory rubber composition which is advantageous in terms of excellent elastic force and impact resistance, capable of being applied to rubber articles, such as tires, shoes and the like.

In accordance with an aspect of the present invention, there is provided a shape memory rubber composition comprising 15-55 % by weight of a crystalline polyalkylene polymer, having trans double bonds comprising 60 % or more of its total double bonds, a melting point (TM) of 28 °C and a glass transition point (Tg) of -80 °C; 40-80 % by weight of a rubbery polymer having crosslinkable points, such as halogen atoms, carboxyl groups or epoxy groups, in polymer principal chains and side chains; 1-10 % by weight of a vulcanizing agent, being not crosslinked with said crystalline polyalkylene polymers but crosslinked with said rubbery polymers; and other additives.

25

BEST MODES FOR CARRYING OUT THE INVENTION

Useful in the present invention, crystalline polyalkylene polymers having a melting point of about 28 °C or higher and a glass transition point of about -80 °C, and having large numbers of double bonds therein, of which
5 trans double bonds constitute 60 % of the total amount of the double bonds. In particular, it is preferred that the crystalline polymers having a crystallinity of 8 % or more at 22 °C, in addition to said properties, are used. The crystalline polyalkylene polymers are used alone or in a
10 mixture of two or more polymers, and preferably have, but are not limited to, a weight average molecular weight of 80,000-200,000.

The crystalline polyalkylene polymers are used in an amount of about 15-50 % by weight on the basis of the
15 total weight of the rubber composition. If the amount is less than 15 % by weight, the shape-recovering rates become slow and the deformation-maintaining ratios at room temperature are decreased. On the other hand, if the amount exceeds 55 % by weight, hardness is very high and
20 elastic force becomes poor.

Additionally, in the rubbery polymers used in the present invention, the functional groups, such as halogen atoms, carboxyl groups or epoxy groups, are contained in polymer principal chains and side chains, through which
25 crosslinked structures can be formed. The rubbery polymers comprise CR, CSM, CPE, Cl-11R, Br-11R, carboxylated NBR, carboxylated SBR, epoxidized NR, and so

on.

The preferred amount of the rubbery polymers ranges from about 40 to 80 % by weight, based upon the total amount of the composition. The amount less than 40 % by weight results in poor elastic force, whereas the amount exceeding 80 % by weight results in slow shape-recovering rates.

The rubber composition of the present invention contains a vulcanizing agent (or a crosslinking agent), which crosslinks not with the double bonds in the crystalline polyalkylene but rather crosslinks with the halogen atoms-containing rubbery polymers. Examples of the vulcanizing agents include metal oxides, such as ZnO, MgO, PbO, Pb₃O₄, etc.; thiourea based compounds; and isocyanate based compounds.

The rubber composition further comprises additives, such as vulcanization accelerators, plasticizers for controlling hardness or softness, fillers, antiaging agents and so on, within the range not impairing the effect of the present invention.

The shape-memory rubber composition is processed through a kneading process to obtain the rubber articles, in which said composition is kneaded at a temperature above the melting point of crystalline polyalkylene polymers, blended and then subjected to vulcanization in finishing machines, such as an injector or an extruder, under high temperature or high temperature and pressure,

to produce the articles. In the case of vulcanization at high temperature or high temperature and pressure, the vulcanizing agents are not reacted with double bonds of crystalline polyalkylene polymers but reacted with the crosslinkable points-containing rubbery polymers, whereby the rubbery polymers having crosslinked structure and the crystalline polyalkylene polymers having not crosslinked structure are mutually penetrated into each polymer chain to obtain an IPN (interpenetrating network) structure, which are interlocked structures. Interpenetrating polymer networks are defined as a blend of two or more polymers where each material forms a continuous network, each network interpenetrating the other, and is therefore a type of polymer/polymer composite, comprising polymeric ingredients which are independently crosslinked. In such structures, the not crosslinked-crystalline polyalkylene polymers are liquefied at their melting points or higher, and crystallized at temperatures below the melting points, in chemically crosslinked rubber phases. The generated crystalline portions are physically crosslinked with the rubbery polymer chains, and thus increase density of the totally crosslinked structures.

The density change of crosslinked structures reflects the shape memorizing performance, which depends on the proportion of the rubbery polymers and the crystalline polyalkylene polymers, a crystallinity and a melting point of the crystalline polyalkylene polymers.

Of these factors, melting points of polyalkylene polymers affect the shape memorizing temperature, which may be thus adjusted when polyalkylene polymers having different melting points are appropriately used.

5 When finished articles prepared from the rubber composition of the present invention through kneading, vulcanizing and finishing processes, are heated to melting points or higher of crystalline polyalkylene polymers to obtain the altered shape of articles, which are then
10 cooled to room temperature to memorize the altered shape of articles, and thereafter warmed to melting points or higher of crystalline polymers by use of hot water or hot air, the original shape of articles is thereby restored.

 A better understanding of the present invention may
15 be obtained in light of the following examples which are set forth to illustrate, but are not to be construed to limit the present invention.

EXAMPLE 1

20 100 parts by weight of CR (PM-40, supplied from Denki Kagaku Kogyo Kabushiki Kaisha, Nippon), 40 parts by weight of crystalline polyalkylene (trans double bonding content: 80 %, melting point: 55 °C, glass transition
25 point: -75 °C, weight average molecular weight: 100,000), 5 parts by weight of ZnO as a vulcanizing agent, 4 parts by weight of MgO and 0.5 parts by weight of stearic acid

as a lubricating agent were kneaded in a roll mill for rubber-kneading at 70 °C at a rotation ratio of 1.25:1. The kneaded composition was vulcanized and pressed at 150 °C and 150 kgf/cm² for 15 minutes, to yield 2.5 mm thick
5 rubber test pieces.

The rubber test pieces were allowed to stand at room temperature for 24 hours, after which their hardness was measured by KSM-6518 vulcanized rubber physical test at room temperature. Then, the test pieces were marked in
10 the intervals of 2 cm, dipped in warm water of 60 °C for 5 minutes and thus reaching an elongation ratio of 100 %, and then dipped in water of 20 °C for 5 minutes.

The test pieces were taken out of water, and let stand at room temperature for 24 hours, and then their
15 deformation-maintaining ratios were measured. After test pieces were dipped in water of 60 °C, the period of time required to restore the original shape was measured. After 5 minutes, deformation restoring ratio was measured. The test piece was introduced into a hot air oven
20 maintained at 60 °C, and allowed to stand for 1 hour, followed by measuring the hardness at 60 °C on iron plate heated to 60 °C. The results are given in Table 1, below.

EXAMPLES 2-4

25

These examples were performed in the same manner as in the above example 1, except that mixing amounts of

crystalline polyalkylene polymers were changed as in the following table 1. The results are shown in Table 1, below.

5

TABLE 1

Component and Properties	Ex.1	Ex.2	Ex.3	Ex.4
CR	100	100	100	100
Polyalkylene	40	60	80	100
Stearic acid	0.5	0.5	0.5	0.5
MgO	4	4	4	4
ZnO	5	5	5	5
Hardness at Room Temp.(Shore A)	63	68	74	82
Deformation-maintaining ratio at room temp.(%)	99	100	100	100
Deformation-restoring ratio after dipping in warm water (%)	100	100	100	100
Deformation-restoring rate (sec)	12	12	12	12
Hardness at 60 °C (Shore A)	43	42	42	41

EXAMPLE 5

10

This example was carried out in the same manner as in Example 1, except that the crystalline polyalkylene polymer was mixed in the amount of 30 parts by weight. The results are presented in Table 2, below.

15

EXAMPLE 6

This example was conducted in the same manner as in the above example 5, except that additives shown in the following table 2 were further used. The results are given in Table 2, below.

20

COMPARATIVE EXAMPLES 1 AND 2

These comparative examples were conducted in the same manner as in the above example 5, except that additives shown in the following table 2 were further used.

5 The results are given in Table 2, below.

EXAMPLE 7

10 This example was conducted in the same manner as in the above example 4, except that carbon black was further added in the amount of 50 parts by weight. The results are given in Table 2, below.

TABLE 2

15

Component and Properties	Ex.5	Ex.6	C.Ex.1	C.Ex.2	Ex.7
CR	100	100	100	100	100
Polyalkylene	30	30	30	30	100
Stearic acid	0.5	0.5	0.5	0.5	0.5
MgO	4	4	4	4	4
ZnO	5	5	5	5	5
Carbon Black		30	5	5	50
Aromatic Oil			90	30	
Foaming agent				10	
Hardness at Room Temp. (Shore A)	58	70	20	13	90
Hardness at 60 °C (Shore A)	44	56	16	4	58
Deformation-maintaining ratio at room temp. (%)	98	99	96	97	100
Deformation-restoring ratio after dipping in warm water (%)	100	100	97	97	100
Deformation-restoring rate (sec)	12	10	24	41	11

INDUSTRIAL APPLICABILITY

20 The shape memory rubber composition of the present invention can be applied to tires, shoes, belts, rubber

hoses, rubber coating rolls, rubber lining, rubber seats,
rubber sponges and so on, and also used for preparation of
rubber products having complex functions, because various
design or performance of products can be obtained by
5 changing the shape of articles.

The present invention has been described in an
illustrative manner, and it is to be understood that the
terminology used is intended to be in the nature of
description rather than of limitation. Many modifications
10 and variations of the present invention are possible in
light of the above teachings. Therefore, it is to be
understood that within the scope of the appended claims,
the invention may be practiced otherwise than as
specifically described.

CLAIMS

1. A shape memory rubber composition comprising:
15-55 % by weight of a crystalline polyalkylene polymer,
5 having trans double bonds comprising 60 % or more of its
total double bonds, a melting point (TM) of 28 °C and a
glass transition point (Tg) of -80 °C;
40-80 % by weight of a rubbery polymer having crosslinkable
points in polymer principal chains and side chains;
10 1-10 % by weight of a vulcanizing agent, being not
crosslinked with said crystalline polyalkylene polymers but
crosslinked with said rubbery polymers; and other additives.

2. The rubber composition as defined in claim 1,
15 wherein the crystalline polyalkylene polymer has a
crystallinity at 22 °C of 8 % or more.

3. The rubber composition as defined in claim 1,
wherein the crystalline polyalkylene polymer has a weight
20 average molecular weight in a range of 50,000 to 200,000.

4. The rubber composition as defined in claim 1,
wherein the crosslinkable points in the rubbery polymer
comprise functional groups, said functional groups being
25 selected from the group consisting of halogen atoms,
carboxyl groups, or epoxy groups.

comprise functional groups, said functional groups being selected from the group consisting of halogen atoms, carboxyl groups, or epoxy groups.

5 5. The rubber composition as defined in claim 1, wherein the rubbery polymer are selected from the group consisting of CR, CSM, CPE, Cl-11R, Br-11R, Carboxylated NBR, Carboxylated SBR and Epoxized NR.

10 6. The rubber composition as defined in claim 1, wherein the vulcanizing agent is selected from the group consisting of metal oxides, thiourea based compounds, and isocyanate based compounds.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR01/00609

A. CLASSIFICATION OF SUBJECT MATTER

IPC7 C08L 23/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7 C08L 23/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean Patents and Applications for Inventions since 1975

Korean Utility Models and Applications for Utility Models since 1975

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

NPS, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 55-152611 A (Bridgestone Corp.) 28 November 1980 see the whole document	1-6
A	US 5,189,110 A (Asahi Kasei Kogyo Kabushiki Kaisha) 23 February 1993 see the whole document	1-6

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 55-152611 A	28.11.80	none	
US 5189110 A	23.02.93	JP 63-323267 A JP 1-284700 A	23.12.88 02.11.89

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